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Ionic Polymers as a New Structural Motif for High Energy-Density Materials

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Supporting Information Placeholder

ABSTRACT: Energetic materials have been used for nearly two centuries in military affairs and to cut labor costs and expedite laborious processes in mining, tunneling, construction, demolition, and agriculture, thereby making a tremendous contribution to the world economy. Yet there has been little advancement in the development of altogether new energetic motifs in spite of long standing research efforts to develop superior materials. We report the discovery of new energetic compounds of exceptionally high energy content and novel polymeric structure which avoid the use of lead and mercury salts common in conventional primary explosives. Laboratory tests indicate the remarkable performance of these nickel- and cobalt-based energetic materials, while DFT calculations indicate that these are possibly the most powerful metal-based energetic materials known to date, with heats of detonation comparable with the most powerful organic-based high explosives currently in use.

The value of harnessing the power of energetic materials has now been realized for quite some time, resulting in their pervasive use in diverse commercial processes.[1] Advancements in energetic materials have also been driven by an understandable need to find more powerful, stable, and reliable materials for military devices. Over the last century, the discovery of new, improved energetic materials has lost pace due to the availability of many acceptable materials and their ongoing optimization. Nevertheless, increasing environmental concerns[2] regarding heavy-metal based primary explosives and rapidly evolving terrorist threats continue to inspire research[3] toward superior energetics.

Beyond commercial considerations, a basic fundamental question in the field of energetic materials remains – just how much energy can be stored in an explosive compound while maintaining practical levels of stability? Energetic compounds generate their power by the rapid decomposition of chemical bonds to form thermodynamic sinks such as CO_2, H_2O, and N_2. Particularly unstable chemical bonds can be considered "loaded" for rapid decomposition, thereby affording better explosive performance. Yet if the bonds are too unstable, they will not be formed in the first place, or the formed compound will be too sensitive to handle. Developing energetic materials with high densities provides another route to improving explosive performance without introducing increased instability. The detonation velocity of a material, and consequently the intensity of its explosion, is proportional to its density. A notable development in this vein was the synthesis of octanitrocubane[4]

(ONC) which is regarded by many as the most powerful chemical explosive to date. ONC was highly desired because the predicted efficient packing of its cube-like molecules would allow for the highest known density for organic explosives. Another explosive considered in the high-energy community has been hexanitrobenzene (HNB).[5] Remarkably, in spite of the direct relationship between solid state structure and explosive performance, single crystal X-ray studies of some of the most famous energetics have only been undertaken comparatively recently.[6]

Energetic metal salts and complexes offer density beyond the reach of regular organic explosives, and a number of metal-based explosives including lead azide, lead styphnate, and mercury fulminate (MF) have been widely used as initiation compounds for many decades. However, the decomposition of metal-ligand bonds typically affords less energy than the decomposition of organic bonds, and metals do not decompose to generate gases like CO_2, N_2, and H_2O, which generate the rapid expansion of an explosion. Hence, these heavy-metal-based explosives have low heats of detonation (ΔH_{det}) per unit mass (kcal/g), and in spite of high densities, the ΔH_{det} per unit volume (kcal/cc) are still only slightly higher than TNT.

We report here the synthesis, structure determination, and computational analysis of cobalt- and nickel-based energetic materials in which bridging ligands join adjacent metal centers to form coordination polymers, a class of materials currently being pursued in diverse applications,[7] but essentially unexplored in the field of energetic materials. By synergizing the effects of high density, weak precursor bonds, and gas production, these new coordination polymers afford energies of detonation beyond those of all other metal-based explosives to date and on par with the most powerful organic secondary explosives in use today.

Furthermore, to our knowledge, there are no other coordination complex structures with hydrazine as the sole inner-sphere ligand, an astounding fact in view of the numerous and familiar examples of hexamine coordination complexes. Examination of hydrazine-containing coordination compound crystal structures in the Cambridge Structural Database and the Inorganic Crystal Structural Database reveal that competing ligands or coordinating anions consistently intrude into the inner coordination sphere of the metal, yielding mixed ligand complexes. There have simply not been reports of crystal structures for metal-hydrazine complexes with non-coordinating anions such as nitrate, perchlorate, tetrafluoroborate, etc. This poses a conspicuous gap in fundamental inorganic structure determination, considering the substantial research activity in the areas of metal organic frameworks (MOFs)[8] and inorganic cages[9]. The design and preparation of such architectures rely on multidentate

ligands and, frequently, non-coordinating anions. Hence, the structures reported here provide a starting point for investigating a hitherto overlooked aspect of coordination chemistry.

Our investigation began with the desire to enhance the performance of an initiation compound, nickel hydrazine nitrate (NHN).[10] While regarded as a viable substitute for commonly used metal azides,[11] it possesses relatively low impact sensitivity for this application. Metal perchlorate salts are generally more sensitive than their corresponding nitrates, and indeed one attempted preparation of nickel hydrazine perchlorate (NHP) resulted in an explosion.[12] In that work, the authors deemed the substance too sensitive for further investigations, and no further reports of this species or its analogues have been made for sixty years. Yet, one abbreviated investigation[12] in which no structural information was obtained should not altogether rule out continued efforts to prepare, study, and utilize metal hydrazine perchlorates. Additionally, it was important to explore whether substituting the Ni-centers with other metals could potentially alter the sensitivity and performance of this class of materials. To this end, we succeeded in preparing and elucidating the structures of nickel hydrazine perchlorate (NHP) and cobalt hydrazine perchlorate (CHP). As shown below, both these materials prove to be immensely powerful primary explosives. NHP and CHP crystallize within one day following the addition of hydrazine to a concentrated aqueous solution of the corresponding metal perchlorate with limited exposure to ambient atmosphere.

As expected, NHP turned out to be highly sensitive. A total of three explosions were observed, first upon grinding, second upon extraction of a 2-3 mg crystal from a vial (the vial was shattered by just this small amount), and third in solution, when an apparently undisturbed vial containing no observable crystalline material exploded without an obvious external stimulus. These observations indicate that NHP has a low critical diameter for detonation. In contrast, CHP could be conveniently initiated by flame, spark, and impact while remaining sufficiently stable for safe handling. CHP responded to a 2.5 kg weight dropped from 20 cm on a drop-hammer apparatus[13] indicating that it is modestly more sensitive than conventionally used explosives.

In spite of obvious difficulties stemming from the high sensitivity (of NHP) and explosive nature of these materials, X-ray single crystal diffraction data were obtained, from which accurate crystal structures were determined. Our analysis indicates that both NHP and CHP crystallize in the monoclinic P2(1)/n space group with two molecules per unit cell and half a molecule per asymmetric unit with very similar unit cell parameters. Both crystals form continuous parallel polymeric chains in which every subsequent metal atom is bridged with the previous one by a single hydrazine molecule (Figure 1, left). Thus the octahedral coordination sphere of each metal consists of six hydrazine molecules; four of these are coordinated in a terminal mode and two are employed for bridging with adjacent metal centers. The perchlorates run parallel to the backbones of the coordination polymers with possible hydrogen bonding between perchlorate oxygens and hydrazine hydrogens with a closest distance of 2.257 Å. Ni-N bond lengths range from 2.124 to 2.178 Å with the shortest bond being associated with the nitrogen atom of the bridging hydrazine unit. Co-N bonds are slightly longer ranging from 2.156 to 2.232 Å with the shortest distance again being the one with a bridging hydrazine molecule. These bond lengths are completely in line with average Ni-N and Co-N bonds for coordination compounds. However, the N-N bond lengths of the bridging hydrazine ligands are elongated to 1.476(2) Å relative to the N-N bond lengths of

1.45±0.01 and 1.46±0.02 Å reported for hydrazine monohydrate[14] and hydrazine,[15] respectively. Since the position of the H-atoms cannot be accurately determined from XRD, we structurally relaxed the H-atoms by density functional theory (DFT) calculations (see below) while keeping the heavy (i.e. non-H) atoms fixed in their XRD-determined positions. The resultant N-H bond-lengths vary between 1.02 and 1.04 Å, in good agreement with an average N-H bond-length of ~ 1.015 Å[16] obtained from neutron-diffraction studies on many organic molecules.

The structure of NHN[10] was also elucidated for the first time, albeit with lesser precision than the NHP and CHP structures. Whereas the perchlorate structures adopt a linear polymeric motif utilizing only one bridging hydrazine, NHN adopts a cage polymer motif in which all hydrazine ligands bridge successive nickel centers (Figure 1, right). Coordination polymer structures have been observed with a single bridging hydrazine in the presence of other co-bridging ligands[17] as have bis(bridging)[18] hydrazine motifs. But NHN represents the first structure of such a tris(bridging) hydrazine cage polymer motif, even though early spectroscopic evidence has suggested such structures are quite general.[19] The structures of NHP and CHP are the only structures yet reported in which a single bridging hydrazine defines the backbone of a coordination polymer. Hence, the structure of NHP, CHP, and NHN demonstrate that hydrazine still possesses untapped structural potential as a bridging bidentate ligand for construction of inorganic architectures, which could yet be explored. Selection of non-coordinating anions such as tetrafluoroborate or hexafluorophosphate, which lack the oxidizing nature of nitrate and perchlorate, may yield interesting structures sans energetic properties.
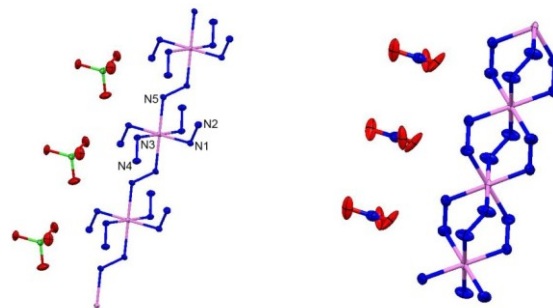

Figure 1: (Left) Crystal structure of nickel hydrazine perchlorate (NHP); Selected bond distances Ni-N1 = 2.136 (1) Å, Ni-N5 = 2.117 (1) Å, N1-N2 = 1.457 (1) Å. Selected bond angles (°) N1-Ni-N3 = 90.84(5), N1-Ni-N5 = 92.42(5). (Right) Structure of nickel hydrazine nitrate (NHN). red = oxygen, green = chlorine, blue = nitrogen, purple = nickel. Ellipsoids are scaled at 50% probability.

Reduced structural reinforcement in the non-bridged polymers, more sensitive perchlorate anion, and higher nitrogen:metal ratio for NHP ($NiN_{10}H_{20}O_8Cl_2$) and CHP ($CoN_{10}H_{20}O_8Cl_2$) are all expected to yield increased power and sensitivity as compared to NHN ($NiN_8H_{12}O_6$). Additional power for the perchlorate materials could also arise from the likely formation of more stable detonation products, i.e., metal-chloride ($NiCl_2$, $CoCl_2$) as opposed to pure metal (Ni) formed by the detonation of NHN (see discussion below).

Given the qualitative observations of NHP and CHP's sensitivity and explosive power, it was natural to seek theoretical estimates of the heats of explosion for these compounds. To this end, first-principles simulations using density functional

theory (DFT) was used to compute the energies of detonation of the geometry-optimized structures ($\Delta E_{DFT, det}$), defined as the difference between the energy of formation of the explosive and that of the detonation products. The computed detonation energies were correlated with the known heats of detonation (ΔH_{det}) for common high explosives (Chart 1). The correlation developed in Chart 1 was then used to estimate the ΔH_{det} of NHN, NHP, and CHP, as displayed in Chart 2, alongside the known values for common energetic materials.

The extended polymeric backbone structures of NHN, NHP and CHP prompted the use of all calculations in periodic supercells representing the smallest repeating unit of the explosive. This procedure also accounts for the contribution of the cohesive energy (i.e. heat of sublimation) of the crystalline solid. The DFT code DMol[3] [20] was employed, in which the electronic wave functions were expanded in a double-numeric polarized (DNP) basis set, while the exchange and correlation effects were incorporated through the gradient-corrected PBE functional.[21] In addition, being a periodic calculation, an accurate Brillouin-zone sampling of the reciprocal lattice was necessary. This was ensured through the summation over a finite set of K-points chosen according to the Monkhorst-Pack scheme[22] with a grid spacing of 0.05 Å^{-1}.
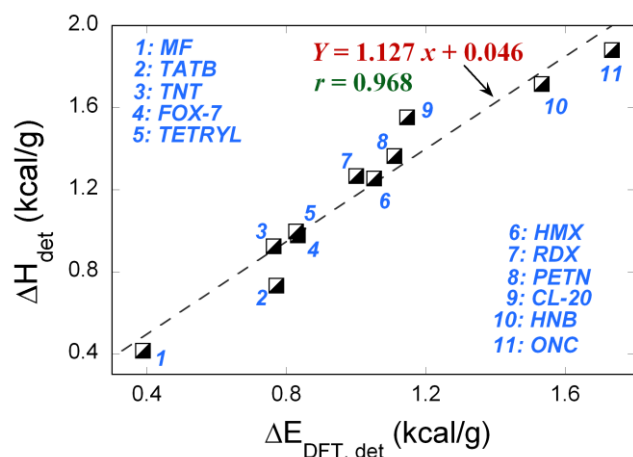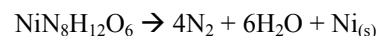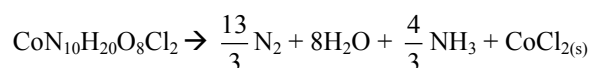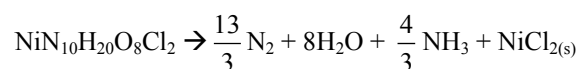

Chart 1: Energy of detonation for DFT-optimized structures ($\Delta E_{DFT, det}$) *vs.* the estimated heat of detonation (ΔH_{det}) from literature for eleven high-explosive materials (HEs). The literature values are taken from ref.[23] for explosives 1 through 9 and ref.[24] for explosives 10 and 11. Abbreviations used: MF (mercury fulminate), ONC (octanitrocubane). The rest are commonly accepted explosive names.

For organic (i.e., C, H, N, and O containing) explosives the detonation products and their relative abundance were determined by state-of-the-art thermochemical calculations using the code CHEETAH.[25] For systems containing metals, the most stable products were assumed under the constraints of stoichiometrically available oxygen, *i.e.*, $NiCl_2$ (solid) for NHP, $CoCl_2$ (solid) for CHP, and Ni (solid) for NHN, respectively. Thus, the complete detonation reactions considered for these explosives were:

$$NiN_{10}H_{20}O_8Cl_2 \rightarrow \frac{13}{3}N_2 + 8H_2O + \frac{4}{3}NH_3 + NiCl_{2(s)}$$

$$CoN_{10}H_{20}O_8Cl_2 \rightarrow \frac{13}{3}N_2 + 8H_2O + \frac{4}{3}NH_3 + CoCl_{2(s)}$$

$$NiN_8H_{12}O_6 \rightarrow 4N_2 + 6H_2O + Ni_{(s)}$$

All non-metal-containing products, including water, were treated as a gas. Chart 1 plots the computed $\Delta E_{DFT, det}$ values versus the corresponding detonation heats ΔH_{det} from the literature.[23-24] The data displays a strong linear correlation ($r = 0.97$), with the corresponding regression curve indicated by the dashed line. Chart 2 uses this correlation to predict the heats of explosion of CHP, NHP and NHN along with the 95% statistical confidence limits.[26] Two important results of note are: (1) the only published ΔH_{det} value for NHN, 1.014 kcal/g (2.16 kcal/cc)[10] is within the error margin, but close to the upper limit of our prediction; (2) CHP and NHP appear to possess similar heats of detonation (with NHP being slightly higher) with the mean predicted value being similar to PETN and RDX, two of the most energetic materials commonly employed. If the actual value is close to the upper 95% confidence limit of our predicted range (as for NHN), the heat of detonation would be even higher, comparable to that of CL-20. Within the metal-containing explosives category, both NHP and CHP clearly appear to be the strongest known primary explosives, with heats of detonation substantially higher than mercury fulminate, lead azide,[23] or NHN.[10]
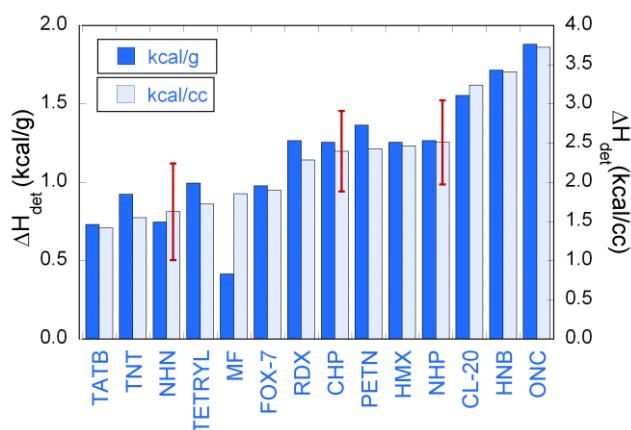

Chart 2: Bar diagram representation of the literature ΔH_{det} values for the eleven HEs along with the predicted ΔH_{det} for NHN, CHP, and NHP using the linear correlation developed in Chart 1. Also indicated are the error margins for the predicted values at the 95% confidence level. Both mass-density (kcal/g) and volume-density (kcal/cc) of the heat of detonation are indicated, and the heats arranged in the increasing order of volume-density (kcal/cc).

The synthesis and structural determination of NHP, NHN, and CHP reveal a new class of ionic polymeric energetic materials, never before observed, comparable with the most powerful explosives in use today. Apart from a traditional detonating role, the low critical diameter indicates that these may be used for microcharges as they can be easily initiated by spark or heat and even quantities of 0.1 mg can release a substantial amount of force. Furthermore, the crystal structures of nickel hydrazine perchlorate, nickel hydrazine nitrate, and cobalt hydrazine perchlorate represent the first examples of coordination complexes with only hydrazine as an inner sphere ligand and even provide the first examples of their respective architectural motifs.

Associated Content

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Notes – Hazard Warning

The materials described in this communication pose extreme explosive hazards, both in terms of sensitivity and explosive power. In the case of nickel hydrazine perchlorate, the material is sufficiently sensitive to preclude effective characterization beyond the isolation of a single crystal for X-ray diffraction. The combination of such extreme sensitivity and unpredictability with its tremendous power make this an exceptionally hazardous material. Cobalt hydrazine perchlorate, though comparatively more stable, is still a sensitive primary explosive and still generates extremely high power output. Even small quantities (<1mg, e.g. a small single crystal) can cause severe physical damage to their surroundings.

Acknowledgment

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Supplemental Information

Hazard Warning and Safety Precaution

The prepared metal hydrazine perchlorate complexes are very powerful energetic substances, capable of initiation by impact, friction, electric spark, heating or open flame. Nickel hydrazine perchlorate is reported to have caused an explosion by introduction of a glass stirring rod into the reaction vessel[1] and caused an accident at Texas Tech University in 2010. Utmost care and use of safety protocols (such as use of face shields, Kevlar gloves and materials least capable of static discharge) should be used at all times. Starting materials also pose danger, as hydrazine hydrate is a known carcinogen and perchloric acid and its salts are powerful oxidants. We strongly discourage any attempt to repeat these preparations on scales larger than described here, as even <1 mg quantities are known to detonate and pose extreme explosive hazard.

Materials

Perchloric acid 60-62%, cobalt perchlorate hexahydrate and nickel perchlorate hexahydrate were obtained from Alfa Aesar, hydrazine hydrate 64% from Acros Organics. All reagents were used without further purification. Syntheses

Syntheses

$NiN_{10}H_{20}Cl_2O_8$ (NHP): Nickel (II) perchlorate-hexahydrate (40 mg, 0.11 mmol) was dissolved in 50 μL of distilled water. 100 μL of hydrazine hydrate (64%, 2 mmol) was added with stirring using a micropipette. Upon addition the solution turned purple. The reaction vial was immediately tightly capped and placed behind a blast shield. The formation of purple crystals of the product began within 24 hours. The product tends to adhere to the walls of the vial necessitating extra care in extracting crystals from the vessel. Extraction should not be attempted with the use of a metal spatula as the friction generated is enough to cause an explosion. Explosion of 2-3 mg of the substance is able to shatter the glass vial and cause tissue damage. Crystals can be removed using a thin plastic object, for example micropipette tip. When the vial was opened and disturbed, the product started precipitating, filling the vial with tightly packed product which stuck to the walls. It was highly problematic to remove it without an explosion which is why the exact yield of the reaction was never recorded.

$CoN_{10}H_{20}Cl_2O_8$ (CHP): Cobalt (II) perchlorate hexahydrate (40 mg, 0.11 mmol) was dissolved in 50 μL of distilled water. 100 μL of hydrazine hydrate (64%, 2 mmol) was added with stirring using a micropipette. Upon addition the solution turned orange-red. The reaction vial was immediately tightly capped and placed behind a blast shield. Formation of orange rhombohedral crystals of the product began within 24 hours. The product tends to adhere to the walls of the vial necessitating extra care in extracting crys-

tals from the vessel. The product was filtered, washed with hydrazine hydrate and air dried on filter paper at room temperature (20 mg, 31% yield). Anal. calc. for $CoN_{10}H_{20}Cl_2O_8$: 418 g/mol N, 33.49; H, 4.78; Found: N, 32.68; H, 4.28. Impact sensitivity was observed at the height of 20 cm and the weight of 2.5 kg. For reference, S3 PETN was determined to have an impact sensitivity of 42 cm with a weight of 2.5 kg on the same instrument.

Drop-hammer and Spark Tests

Sensitivity data was obtained by use of a home-made drop-hammer.[2] The instrument consists of a metal bar to which various weights can be attached. The bar is held at a user-specified height by an electromagnet; when the electromagnet is switched off, the bar and the weight will fall upon a flat metal surface which holds the compound of interest. Thus the weight attached to the bar and the height from which it falls can be conveniently controlled to determine the impact sensitivity of a given compound.

Electric spark test was performed using a High Frequency Generator, Model BD-10AS Electro-Technic Products, at 115 V and 0.35 A.

Thermal Analyses

Thermal analyses of NHP and CHP presented considerable practical challenges. Efforts began with the less sensitive, but similarly powerful, CHP. In a first attempt to acquire a DSC trace for CHP, 0.7 mg of material in a sealed aluminum pan damaged the instrument, necessitating the purchase of a new furnace. Thereafter, very small samples of CHP (0.050, 0.072, 0.071 mg, measured using the TGA balance) were used in DSC experiments, using a perforated lid. A typical result is shown in Figure S1. Under these circumstances, a single exotherm is reproducibly (×3) observed with a peak position between 187-193°C evolving 1.96 ± 0.08 kJ/g. No melting endotherm was observed. Any consideration of the heat evolved must be qualified by the fact that the pan lid was perforated, so gaseous material was free to escape during the data collection. The somewhat broad temperature range observed for the peak positions from sample to sample likely arises from the fact that each sample consisted of a single crystal of very low mass which is significantly lower than is usually needed for accurate analysis.

In view of the challenges encountered in the characterization of CHP and of the high sensitivity of NHP, attempted thermal characterization of NHP poses unjustifiable risk to personnel and equipment, and would likely yield damage before any useful result. In the case of nickel hydrazine nitrate (NHN) Talawar et al. reported: "Differential scanning calorimetry (DSC) of NiHN revealed a violent reaction at 220°C followed by explosion, leading to abnormal curve".[3] This data was collected at a ramp rate of 5°C/min under nitrogen flow.
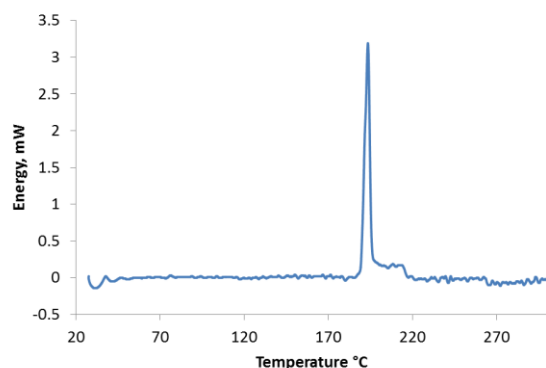
Figure S1 Differential Scanning Calorimetry thermogram of CHP (0.071 mg) with a perforated lid, ramp rate of 5°C/min under nitrogen. Peak 193.5°C, Onset 186.5°C, Endset 199.8°C. Heat evolved 137.0 mJ; 1.93kJ/g.

Data Collection and Analyses

Table S1 Data collection and refinement statistics summary

	Nickel Hydrazine Nitrate (NHN)	Nickel Hydrazine Perchlorate (NHP)	Cobalt Hydrazine Perchlorate (CHP)
CCDC number	842079	842080	842078
Formula	$Ni(N_2H_4)_3(NO_3)_2$	$Ni(N_2H_4)_3(ClO_4)_2$	$Co(N_2H_4)_3(ClO_4)_2$
Density (g/cm³)	2.156	1.983	1.948
Data Collection			
Crystal System	trigonal	monoclinic	trigonal
Space Group	P-3c1	P2(1)/n	P2(1)/n
Color and Shape	purple plates	purple plates	orange rhombohedrum
Cell Dimensions			
a, b, c (Å)	8.117(15), 8.117(15), 7.531(14)	5.1131(15), 16.2669(15), 8.5573(8)	5.1719(3), 16.3158(11), 8.5974(6)
$\alpha\beta\gamma$ (°)	90, 90, 120	90, 100.487(1), 90	90, 100.7380(10), 90
Volume (Å³)	429.70(14)	699.86(11)	712.78(8)
Z	2	2	2
Resolution (°)	27.40	27.10	26.73
R_{merge}	.0903	0.0224	0.0248
Completeness (%)	99.7	100	100
Redundancy (collected reflections /independent reflections)	6.5 (2178/332)	5.1 (7870/1545)	5.2 (7948/1524)
Refinement			
Data/restraints/parameters	332 / 2 / 30	1545 / 10 / 127	1524 / 10 / 127
Goodness of fit on F^2	1.089	1.049	1.063
Final R indices [I>2σ (I)]	R1 = 0.0470, wR2 = 0.1185	R1 = 0.0195, wR2 = 0.0484	R1 = 0.0216, wR2 = 0.0521
R indices (all data)	R1 = 0.0549, wR2 = 0.1253	R1 = 0.0207, wR2 = 0.0491	R1 = 0.0250, wR2 = 0.0536
Largest diff. peak and hole (e. Å⁻³)	0.431, -0.692	0.315, -0.358	0.346, -0.343

Complete supplemental information for these crystal structures is available in the Crystallographic Information files (.cif files) from the Cambridge Crystallographic Data Centre using the accession codes listed above.

Elemental analysis was performed on PerkinElmer 2400 Series II CHNS/O Analyzer. X-ray diffraction data was obtained on Bruker Smart Apex II single-crystal Xray diffractometer at 150 K or room temperature. Multi-scan absorption correction (SADABS) was applied. Structures were solved by direct methods algorithm and refined using SHELX-97 software. All hydrogen atoms were calculated from the electron density map. A data summary for NHN, NHP, and CHP is included below in Table S1. CCDC-842078 (CHP), 842079 (NHN), and 842080 (NHP) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
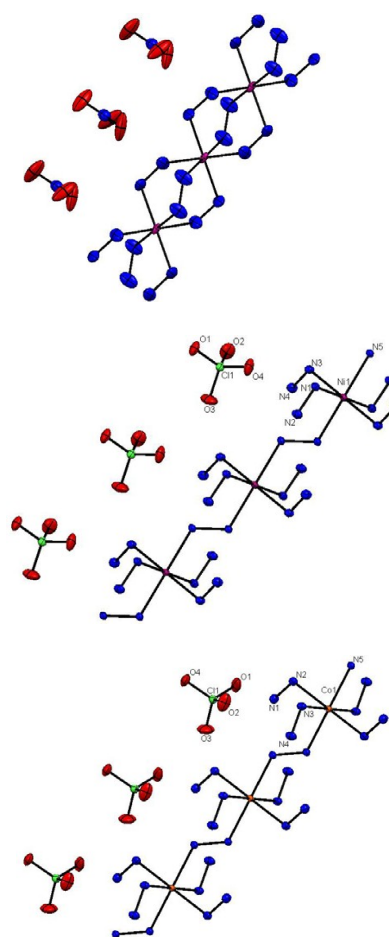

Figure S2 Structure drawing of NHN (top), NHP (center) and CHP (bottom). Ellipsoids are drawn at 50% probability.

Table S2. Energy of formation (ΔE_f), detonation pressure (P_{det}) at the C-J point, and detonation (shock) speed (v_{det}) of NHN, CHP, and NHP. ΔE_f was computed by the DFT code DMol³, while P_{det} and v_{det} were computed using the thermochemical code CHEETAH.

Explosive	ΔE_f (kcal/g)	P_{det} (at C-J Point) (GPa)	v_{det} (km/s)
NHN ($\rho = 1.7$ g/cm³)	-0.60	20.2	7.3[‡]
CHP	-0.20	25.1-33.6*	7.5-9.0*
NHP	-0.21	36.8**	9.2**

[‡]Experimental value: 7.0 km/s.[4]
*Depends on the actual detonation products, *e.g.*, the relative amounts of pure metal (high value) and metal-chloride (low value).
**Corresponds to pure metal as the detonation product; nickel chloride equation of state is not in the current version of CHEETAH and thus not considered for P_{det} and v_{det} estimation.

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